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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a curable composition not causing stringiness in use, having a small slump in an uncured state, excellent weather resistance for a long period of time after curing and a sufficiently high degree of lightening.

SOLUTION: This curable composition is characterized by comprising an oxyalkylene polymer containing a reactive silicon group represented by general formula (1) $-\text{SiXaR}_1(3-a)\dots(1)$ [R1 is a monofunctional organic group; X is a hydroxy group or a hydrolyzable group; a is 1-3] and a polymer containing a (meth)acrylic acid alkyl ester monomer unit and minute hollow bodies of organic resin.

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CLAIMS

[Claim(s)]

[Claim 1] An oxyalkylene polymer (A) which has a reactive silicon group expressed with a following general formula (1), and $-SiX_n R^1_{(3-n)}$ -- (1)

A univalent organic group of the carbon numbers 1-20 in which R^1 may have a substituent, and X show a hydroxyl group or a hydrolytic basis among [type, and a shows an integer of 1-3, respectively. However, when R^1 may be the same respectively or it may differ, when two or more R^1 exist, and two or more X exists, X may be the same respectively or may differ.]

A hardenability constituent comprising:

(Meta) A polymer (B) including an acrylic-acid-alkyl-ester monomeric unit

An organic resin minute hollow body (C).

[Claim 2] The hardenability constituent according to claim 1, wherein said oxyalkylene polymers (A) are 6000 or more number average molecular weights and a 1.7 or less molecular weight distribution (Mw/Mn) oxyalkylene polymer.

[Claim 3] The hardenability constituent according to claim 1 or 2 being a polymer characterized by comprising the following.

A carbon number of an alkyl group of said polymer (B) is an acrylic-acid-alkyl-ester (meta)

monomeric unit of 1-8 as an acrylic-acid-alkyl-ester (meta) monomeric unit.

An acrylic-acid-alkyl-ester monomeric unit whose carbon number of an alkyl group is ten or more (meta).

[Claim 4] The hardenability constituent according to any one of claims 1 to 3 said polymer's (B's)'s being a polymer including an acrylic-acid-alkyl-ester (meta) monomeric unit, and being a polymer which has a reactive silicon group expressed with the above-mentioned general formula (1).

[Claim 5] The hardenability constituent according to any one of claims 1 to 4, wherein said organic resin minute hollow body (C) is a polyvinylidene chloride system resin minute hollow body.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a hygroscopic-surface-moisture hardening type hardenability constituent suitable as the main ingredients, such as sealant and adhesives, in more detail about a hardenability constituent.

[0002]

[Description of the Prior Art]The oxyalkylene polymer which has reactive silicon groups, such as alkoxy silyl groups, (it is hereafter called a "hardened type oxyalkylene polymer"). It can hardened also at a room temperature with the hygroscopic surface moisture in the air, and since the hardened material which has rubber elasticity is obtained and after hardening is excellent also in the adhesive property over various adherends, it is widely used as sealant, adhesives, base resin of the constituent for covering / seal, etc.

[0003]However, when such a hygroscopic-surface-moisture hardening type oxyalkylene polymer is applied, for example to sealant, under the exposure condition in the outdoors, a white bluish mark and a crack may arise on the hardened material surface, and improvement in weatherability is called for.

[0004]As a method of raising the weatherability of a hardened type oxyalkylene polymer, For example, the method indicated by JP,59-78223A, JP,59-122541A, JP,60-31556A, JP,63-112642A, JP,6-172631A, etc. is known. According to these gazettes, it is supposed by making a hardened type oxyalkylene polymer contain the acrylic-acid-alkyl-ester system polymer which has a reactive silicon group (meta) that improvement in weatherability can be aimed at.

[0005]To the hardened type oxyalkylene polymer containing the acrylic-acid-alkyl-ester system polymer which has a reactive silicon group (meta). The presentation which furthermore added bulking agents, such as glass balloons, is indicated by JP,5-86325A as an example, and is indicated [that a weight saving, saving resources, rust prevention vibration proof, etc. are realizable and] by using the presentation concerned as a coating agent for vehicles.

[0006]

[Problem(s) to be Solved by the Invention]However, when it used for the use of sealant, adhesives, etc. in addition to the presentation of an indication being still insufficient for JP,5-86325A in the point of a weight saving, there was a problem that it was [that it is easy to produce a cobwebbing at the time of use] inferior to workability. When it was especially used for a joint part as sealant, there was a problem that a slump (lappet) was large.

[0007]This invention is made in view of the problem of the above-mentioned conventional technology, and is a thing.

does not occur, but the slump of the purpose at the time of un-hardening is small, is excellent also in the weatherability over the long period of time after hardening, and it is that the degree of a weight saving also provides a hardenability constituent high enough further.

[0008]

[Means for Solving the Problem]By using an organic resin minute hollow body as a bulking agent added to a hardened type oxyalkylene polymer containing an acrylic-acid-alkyl-ester (meta) system polymer as a result of repeating research wholeheartedly that this invention persons should attain the above-mentioned purpose, It found out that cobwebbing prevention which was not able to be attained, reduction of a slump, weatherability, and all the four characteristics of a weight saving could

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be attained in a presentation of an indication in the above-mentioned gazette, and this invention was completed.

[0009]Namely, an oxyalkylene polymer (A) in which a hardenability constituent of this invention has a reactive silicon group expressed with a following general formula (1) and $-SiX_g R^1_{(3-a)} \dots (1)$

A univalent organic group of the carbon numbers 1-20 in which R^1 may have a substituent, and X show a hydroxyl group or a hydrolytic basis among [type, and a shows an integer of 1-3, respectively. However, when R^1 may be the same respectively or it may differ, when two or more R^1 exist, and two or more X exists, X may be the same respectively or may differ. A polymer (B) including [meta] acrylic-acid-alkyl-ester monomeric unit and an organic resin minute hollow body (C) are included. [0010]As for an oxyalkylene polymer (A) in this invention, it is preferred that they are 6000 or more number average molecular weights and a 1.7 or less molecular weight distribution (Mw/Mn) oxyalkylene polymer.

[0011]A polymer (B) in this invention as an acrylic-acid-alkyl-ester (meta) monomeric unit, it is preferred that a carbon number of an alkyl group is a polymer including an acrylic-acid-alkyl-ester (meta) monomeric unit of 1-8 and an acrylic-acid-alkyl-ester monomeric unit whose carbon number of an alkyl group is ten or more (meta). As for a polymer (B), it is preferred that it is a polymer including an acrylic-acid-alkyl-ester (meta) monomeric unit, and is a polymer which has a reactive silicon group expressed with the above-mentioned general formula (1). As for an organic resin minute hollow body (C) in this invention, it is preferred that it is a polyvinylidene chloride system resin minute hollow body.

[0012]

[Embodiment of the Invention]First, the oxyalkylene polymer (A) in this invention is explained. The oxyalkylene polymer (A) in this invention is an oxyalkylene polymer which has the reactive silicon group provided with the hydroxyl group or the hydrolytic basis. As the hydrolytic basis concerned, for example, a halogen atom, an alkoxy group, an acyloxy group, an alkenyloxy group, an amino group, a KETOKISHI mate group, an aminoxy group, a carbanoyl group, and a sulfinydril group can be mentioned, and an alkoxy group is especially preferred.

[0013]As the above-mentioned alkoxy group, the alkoxy group of the carbon numbers 1-6 is preferred. It is more preferred that it is 1-4, as such a basis, a methoxy group, an ethoxy group, a propoxy group, and a butoxy group are mentioned, and the carbon number of an alkoxy group has especially a preferred methoxy group. R^1 is a univalent organic group of the carbon numbers 1-20, even if the organic group concerned has a substituent, it is not necessary to have it but, and it is preferred not to have a substituent. As for the carbon number of R^1 , it is preferred that it is 1-16, and it is more preferred that it is 1-8.

[0014]When R^1 is a univalent organic group which does not have a substituent, the organic group concerned may have straight chain shape and which a branched state and annular structure. As such an organic group, an alkyl group, a cycloalkyl group, an aryl group, and an aralkyl group are mentioned, for example. As an alkyl group, the alkyl group of the carbon numbers 1-4 is preferred, and a methyl group, an ethyl group, a propyl group, and a butyl group are mentioned as such an alkyl group. When R^1 is a univalent organic group which has a substituent, the kind in particular of the substituent concerned is not restricted.

[0015]In the reactive silicon group, when two or more basis or organic group R^1 expressed with X exist, they may be the same respectively or may differ. From a viewpoint of promoting bridge construction of an oxyalkylene polymer, as for the number (a in a general formula (1)) of X, it is preferred that it is 2 or 3, and it is more preferred that it is 2. The basis which is not bulky as R^1 is preferred, and a methoxy group is preferred as a hydrolytic basis. Therefore, especially in this invention, a methyl dimethoxy silyl group and a trimethoxysilyl group are preferred as a reactive silicon group.

[0016]The oxyalkylene polymer (A) in this invention has a reactive silicon group expressed with the general formula (1) explained above into the molecule of an oxyalkylene polymer. Here, neither the number of the reactive silicon groups per oxyalkylene polymer monad nor the binding site in particular of the reactive silicon group in an oxyalkylene polymer is restricted. That is, the oxyalkylene polymer (A) should just have the above-mentioned reactive silicon group one or more per monad, and the

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existence part may be both an end of an oxyalkylene polymer, a side chain, an end and a side chain, and *****.

[0017] The oxyalkylene polymer which has a reactive silicon group should just be a polymer which has oxyalkylene as a repeating unit, and oxyalkylene may consist only of one sort and may consist of two or more sorts. Especially when a repeating unit consists of two or more sorts of oxyalkylene. Even if each oxyalkylene connects at random and forms the random polymer of oxyalkylene, oxyalkylene of an identical kind may collect and connect with block like shape, and may form the block copolymer.

[0018] The oxyalkylene polymer may have chemical structure other than oxyalkylene as a repeating unit in the molecule. Since it is common to make cyclic ether react to an initiator (initiator), and to compound as for an oxyalkylene polymer so that it may mention later, it may have a functional group of initiator origin in the molecule. Since the hydroxyl group to contain may be made to react to other functional groups and polymers quantification may be carried out, the oxyalkylene polymer may have in the molecule combination (for example, urethane bond etc.) which a hydroxyl group and other functional groups reacted and produced, so that it may mention later.

[0019] As for the oxyalkylene polymer (A) in this invention, it is preferred that it is what is obtained by using as a raw material the oxyalkylene polymer which has a functional group, and making a part or all of the functional group, and the compound which has a reactive silicon group expressed with a general formula (1) react. As an oxyalkylene polymer which has a reactive silicon group for introducing a reactive silicon group, an oxyalkylene polymer with a hydroxyl group, an unsaturation group, and an isocyanate group as a functional group is mentioned.

[0020] In this invention, it is preferred to use the oxyalkylene polymer (henceforth a "hydroxyl group and oxyalkylene polymer") which has a hydroxyl group at the end as an oxyalkylene polymer which has a functional group for introducing a reactive silicon group. A hydroxyl group end oxyalkylene polymer uses active hydrogen containing compounds, such as univalent, [polyhydric alcohol or univalent], or polyvalent carboxylic acid, as an initiator. Ring opening polymerization of the cyclic ether, such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, and a tetrahydrofuran, can be carried out, and it can be obtained. In this case, alkaline metal cyanide as a potassium system compound and a caesium system compound, a composite metal cyanide complex catalyst, and a metalloporphyrin catalyst can be used as a polymerization catalyst.

[0021] It is preferred to use the multivalent active hydrogen containing compounds which have 2-8 active hydrogen as the above-mentioned initiator, and it is more preferred to use the multivalent active hydrogen containing compounds which have 2-6 active hydrogen. As for the number of active hydrogen, in this invention, since the hardenability constituent which is excellent in the pliability after hardening and an adhesive property is obtained, it is still more preferred that it is 2 or three pieces.

As multivalent active hydrogen containing compounds, polyhydric alcohol is preferred.

[0022] When an alkaline metal catalyst is used as a polymerization catalyst of a hydroxyl group end oxyalkylene polymer. Since the polymer of low molecular weight is obtained comparatively, terminal hydroxyl groups of the polymer concerned is made into sodium alcoholate etc., by making many halogenated compounds, such as a methylene chloride, react, it can quantify many and polymers quantification can be carried out (JP 62-240320, A). On the other hand, as a polymerization catalyst, when a composite metal cyanide complex catalyst is used, the polymer of the amount of polymers and narrow molecular weight distribution can obtain (JP 3-72527, A).

[0023] As for the polymerization catalyst used in order to obtain a hydroxyl group end oxyalkylene polymer, in this invention, it is preferred that it is a composite metal cyanide complex catalyst. The complex which uses zinchexacyano cobaltate as the main ingredients as a composite metal cyanide complex is preferred.

[0024] As a hydroxyl group end oxyalkylene polymer, the polyoxypropylene polyol of 2-6 value is preferred, and polyoxypropylene diol and polyoxypropylene triol are especially preferred. Hydroxyl group end oxyalkylene polymers may be two or more sorts of mixtures in which a molecular weight differs from chemical structure, and adjustment of the physical properties after hardening and the adjustment of the hardening characteristic of them are attained by using such a mixture.

[0025] By using the hydroxyl group end oxyalkylene polymer explained above, the oxyalkylene polymer (A) which has a reactive silicon group by following (i) - the method of (iv) can be obtained, for example.

(i) A method to which the unsaturation group concerned and hydrosilyl compound are made to react

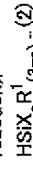
after changing the terminal hydroxyl groups of a hydroxyl group end oxyalkylene polymer into an unsaturation group.

(ii) A method to which a hydroxyl group end oxyalkylene polymer and an isocyanate group content silicon compound are made to react.

(iii) A method to which the isocyanate group concerned and an active hydrogen content silicon compound are made to react after changing the terminal hydroxyl groups of a hydroxyl group end oxyalkylene polymer into an isocyanate group.

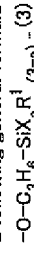
(iv) How to make a sulfinic acid group content silicon compound react to the unsaturation group concerned after changing the terminal hydroxyl groups of a hydroxyl group end oxyalkylene polymer into an unsaturation group.

[0026] (i) In a method, make the compound which has a hydroxyl group, a reactant functional group, and an unsaturation group react to the terminal hydroxyl groups of the hydroxyl group end oxyalkylene polymer obtained by the above-mentioned method, and introduce an unsaturation group into the end of an oxyalkylene polymer first, for example. Subsequently, the reactive silicon group expressed with a general formula (1) can be introduced by, for example, making the hydrosilyl compound expressed with a following general formula (2) react to this polymer (hydrosilylation reaction).



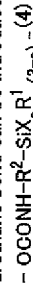
R^1 , X, and a are synonymous with said R^1 , X, and a among [type.]

[0027] As the above-mentioned unsaturation group, an alkenyl group, an acrylyl group, a methacrylyl group, etc. are mentioned. As a hydroxyl group and a reactant functional group, a halogen atom, a carboxyl group (or halo formyl group), an isocyanate group, etc. are mentioned, and when these functional groups react to terminal hydroxyl groups, an ether bond, an ester bond, and a urethane bond are formed, respectively. For example, when the hydrosilyl compound expressed with the above-mentioned general formula (2) is made to react after changing the terminal hydroxyl groups of an oxyalkylene polymer into an allyloxy group, terminal hydroxyl groups turns into a basis expressed with a following general formula (3).



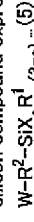
R^1 , X, and a are synonymous with said R^1 , X, and a among [type.]

[0028] (ii) In a method, for example by making a hydroxyl group end oxyalkylene polymer and an isocyanate group content silicon compound react. As shown in a following general formula (4), the reactive silicon group expressed with the end of an oxyalkylene polymer by a general formula (1) via a urethane bond can be introduced.

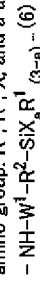


R^2 shows the divalent hydrocarbon group of the carbon numbers 1-20 among [type. R^1 , X, and a are synonymous with said R^1 , X, and a.]

[0029] (iii) In a method, for example, make a hydroxyl group end oxyalkylene polymer and a polyisocyanate compound react on the conditions to which an isocyanate number of equivalent becomes larger than the number of hydroxyl equivalents, and change the terminal hydroxyl groups of a hydroxyl group end oxyalkylene polymer into an isocyanate group first. Next, the reactive silicon group expressed with the end of an oxyalkylene polymer by a general formula (1) as shown in a following general formula (6) can be introduced by, for example, making the active hydrogen content silicon compound expressed with a following general formula (5) react to this polymer.

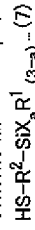


W shows among [type the active hydrogen containing group chosen from the group which consists of a hydroxyl group, a carboxyl group, a sulfinic acid group, the 1st class amino group, and the 2nd class amino group. R^2 , R^1 , X, and a are synonymous with said R^2 , R^1 , X, and a.]



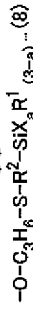
W^1 shows among [type the divalent basis chosen from the group which consists of $-\text{COO}-$, $-\text{CO}-$, $-\text{COS}-$, $-\text{CONH}-$, and $-\text{CONW}^2-$. However, W^2 shows a univalent organic group and R^2 , R^1 , X, and a are synonymous with said R^2 , R^1 , X, and a.]

[0030] (VI) Change the end of an oxyalkylene polymer into an unsaturation group first by the method of a statement in a method at the above-mentioned (I) using a hydroxyl group end oxyalkylene polymer, for example. Subsequently, the reactive silicon group expressed with the end of an oxyalkylene polymer by a general formula (1) can be introduced by making the sulfhydryl group content silicon compound expressed with this polymer and a following general formula (7) react.



R^2 , R^1 , X, and a are synonymous with said R^2 , R^1 , X, and a among [type.]

[0031] (VII) In a method, when the sulfhydryl group content silicon compound expressed with the above-mentioned general formula (7) is made to react after changing the terminal hydroxyl groups of an oxyalkylene polymer into an allyloxy group, terminal hydroxyl groups turns into a basis expressed with a following general formula (11).



R^2 , R^1 , X, and a are synonymous with said R^2 , R^1 , X, and a among [type.]

[0032] The method of the above-mentioned (I) is the method of transforming the unsaturation group concerned, after using terminal hydroxyl groups of a hydroxyl group end oxyalkylene polymer as an unsaturation group, but the following methods are possible for it as a modification mode of this method.

[0033] Namely, in the case where carry out ring opening polymerization of the cyclic ether, and a hydroxyl group end oxyalkylene polymer is obtained under existence of an initiator. As cyclic ether, by using together unsaturation group content monooxide, such as allyl glycidyl ether, glycidyl acrylate, and glycidyl methacrylate. An unsaturated bond can be introduced into the side chain of a hydroxyl group end oxyalkylene polymer (JP 3-79627A).

[0034] Since an oxyalkylene polymer with an unsaturation group is obtained by an end and the side chain by changing the terminal hydroxyl groups of this hydroxyl group end oxyalkylene polymer into an unsaturation group like the method of the above-mentioned (I). The unsaturation group in the polymer concerned can be changed by the same method as the above-mentioned (I), and the oxyalkylene polymer which has a reactive silicon group expressed with an end and a side chain by the above-mentioned general formula (1) can be obtained.

[0035] The method of further the following is also possible as a modification mode of the above-mentioned (I). Namely, by using a compound with an active hydrogen group like allyl alcohol, and an unsaturation group, for example as active hydrogen containing compounds which are the initiators in the case of obtaining an oxyalkylene polymer. The oxyalkylene polymer which has an unsaturation group and terminal hydroxyl groups, such as an allyl end polyoxypropylene monoox, can obtain. After changing the terminal hydroxyl groups of the polymer concerned into an unsaturation group by the same method as the above-mentioned (I) and using all the functional groups of an oxyalkylene polymer as an unsaturation group, by the still more nearly same method as the above-mentioned (I). The reactive silicon group expressed with the above-mentioned general formula (1) by the oxyalkylene polymer can be introduced.

[0036] The oxyalkylene polymer (A) explained above forms a hardenability constituent with a polymer (B) and organic resin minute hollow body (C) including an acrylic-acid-alkyl-ester (meta) monomeric unit. This hardenability constituent can be used as a raw material of sealant or elastic adhesives so that it may mention later. In such a use, in order to have to apply to adhere before a hardenability constituent hardens, moderate workability is required and it is preferred that the viscosity in a room temperature is low for that purpose. As for after hardening, it is preferred to have rupture stress moderate as sealant or elastic adhesives and the degree of breaking extension.

[0037] Therefore, as for the viscosity of the viewpoint of workability to an oxyalkylene polymer (A), in this invention, it is preferred in 25 °C that it is below 30 Pa and s. Although the minimum in particular of viscosity is not restricted, 1 or more Pa-s is preferred, and 5 or more Pa-s is more preferred. When the viscosity of an oxyalkylene polymer (A) exceeds 30 Pa-s, it is in the tendency for the workability of the hardenability constituent obtained to worsen.

[0038] As for an oxyalkylene polymer (A), in this invention, it is preferred that they are more than number average molecular weight (Mn) 6000 and a 1.7 or less (namely, 1.0-1.7) molecular weight distribution (Mw/Mn) oxyalkylene polymer. As for Mn of an oxyalkylene polymer (A), it is preferred from the rupture stress of a hardened material, and a viewpoint of the degree of breaking extension

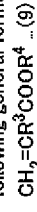
that it is 6000-50000, and it is more preferred that it is 8000-30000. When using the hardenability constituent which viscosity becomes high, for example, is obtained when Mn exceeds 50000 as sealant or elastic adhesives, it is in the tendency for workability, such as extrusion nature, to fall. On the other hand, the hardenability of a constituent tends to be inferior when Mn is less than 6000.

[0039] As for Mw/Mn of an oxyalkylene polymer (A), it is more preferred that it is 1.6 or less, and it is still more preferred that it is 1.5 or less. When Mw/Mn of an oxyalkylene polymer (A) exceeds 1.7, it is in the tendency for the cure rate of the hardenability constituent obtained to fall. This is based on as for an oxyalkylene polymer (A), a cure rate becoming slow when the molecular weight is small. Namely, an average molecular weight is the same oxyalkylene polymer (A). When Mw/Mn compares 1.7 or less thing with the thing in which Mw/Mn exceeds 1.7, since that in which Mw/Mn exceeds 1.7 has large molecular weight distribution, there is much content of a low molecular weight constituent, therefore it is in the tendency for a cure rate to fall. The narrow oxyalkylene polymer (A) of the molecular weight distribution whose value of Mw/Mn is 1.7 or less can be obtained by, for example, using the composite metal cyanide complex mentioned above as a cyclic ether ring opening polymerization catalyst.

[0040] Mn in this invention means the number average molecular weight of the styrene conversion measured by gel permeation chromatography (GPC) with a tetrahydrofuran solvent, and means Mn before hardening about Mn of an oxyalkylene polymer (A). In this invention, Mw/Mn is the value which ** (ed) Mw (weight average molecular weight) of the styrene conversion measured by GPC with a tetrahydrofuran solvent from Mn (number average molecular weight) measured on the same conditions.

[0041] Next, a polymer (B) including the acrylic-acid-alkyl-ester (meta) monomeric unit in the hardenability constituent of this invention is explained. With a polymer including the acrylic-acid-alkyl-ester monomeric unit in this invention (meta). (Meta) The polymer which has a repeating unit which consists of acrylic acid alkyl ester is meant, and the polymer concerned can be obtained by usually polymerizing the unsaturation group content monomer which uses an acrylic-acid-alkyl-ester (meta) monomer as an essential ingredient. In this invention, with an unsaturation group content monomer, it is a compound which has an unsaturated bond (preferably carbon-carbon double bond), the compound which can form a polymer is said, and acrylic acid alkyl ester (meta-) means acrylic acid alkyl ester or methacrylic acid alkyl ester.

[0042] The acrylic-acid-alkyl-ester monomer in this invention (meta) can be expressed with a following general formula (9).



As for R^3 , a hydrogen atom or a methyl group, and R^4 show an alkyl group among [type.]

[0043] Although R^4 in a general formula (9) is an alkyl group, in this invention, a substituted alkyl group with which at least one of the hydrogen atoms of an alkyl group was replaced by hydrocarbon groups, such as cyclic hydrocarbon groups, shall also be included in an alkyl group like an alkyl group and a cycloalkyl alkyl group. The carbon number in particular of an alkyl group is not restricted.

[0044] Even if the polymer (B) in this invention has a repeating unit which consists of one sort of acrylic-acid-alkyl-ester monomers (meta) which are expressed with the above-mentioned general formula (9), or two sorts or more. One sort of acrylic-acid-alkyl-ester monomers or two sorts or more (meta) which are expressed with the above-mentioned general formula (9). It may have a repeating unit which consists of one sort of unsaturation group content monomers other than the monomer concerned, or two sorts or more, and the kind or number of repeating units in a polymer (B) are not restricted in a limitation including the repeating unit which consists of an acrylic-acid-alkyl-ester (meta) monomer. As for the rate of the acrylic-acid-alkyl-ester (meta) monomer in a total monomer, it is preferred to exceed 50 mass %, and it is preferred. [of more than 70 mass %]

[0045] A polymer (B) in this invention as an acrylic-acid-alkyl-ester (meta) monomeric unit, it is preferred that the carbon number of an alkyl group is a polymer including the acrylic-acid-alkyl-ester (meta) monomeric unit of 1-8 and the acrylic-acid-alkyl-ester monomeric unit whose carbon number of an alkyl group is ten or more (meta). That is, as for a polymer (B), it is preferred to have both the repeating unit which the carbon number of an alkyl group becomes from the acrylic-acid-alkyl-ester (meta) monomer of 1-8, and the repeating unit which consists of an acrylic-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). (Meta) It is in the tendency

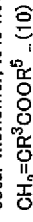
whose characteristics, such as intensity after hardening of the hardenability constituent which the compatibility over the oxyalkylene polymer (A) of a polymer (B) improves, therefore is obtained, improve by using such a combination as an acrylic-acid-alkyl-ester monomer. As an acrylic-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). The acrylic-acid-alkyl-ester (meta) monomer of 10-30 has a more preferred carbon number of an alkyl group, and the acrylic-acid-alkyl-ester (meta) monomer of 10-22 has a still more preferred carbon number of an alkyl group.

[0046] The carbon number of an alkyl group as an acrylic-acid-alkyl-ester (meta) monomer of 1-8, for example, methyl acrylate (meta), ethyl acrylate (meta), acrylic acid (meta) propyl, butyl acrylate (meta), acrylic acid (meta) hexyl, acrylic acid (meta) octyl, 2-ethylhexyl acrylate (meta), and acrylic acid (meta) benzyl are mentioned.

[0047] As an acrylic-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). For example, decyl acrylate (meta), acrylic acid (meta) dodecyl, (meta) Acrylic acid tetradecyl, acrylic acid (meta) hexadecyl, acrylic acid (meta) octadecyl, cicosanyl acrylate (meta), acrylic acid (meta) docosa nil, and acrylic acid (meta) hexacosyl are mentioned.

[0048] In the case where the carbon number of an alkyl group uses together the acrylic-acid-alkyl-ester (meta) monomer of 1-8, and the acrylic-acid-alkyl-ester monomer whose carbon number of an alkyl group is ten or more (meta). Although the ratio in particular is not restricted, as for the former/latter, it is preferred that it is 95 / 5 - 40/60 in a mass ratio, and it is more preferred that it is 95 / 5 - 40/60.

[0049] The polymer (B) in this invention may include unsaturation group content monomeric units other than the monomeric unit concerned other than an acrylic-acid-alkyl-ester monomeric unit, as mentioned above (meta). (Meta) Although the compound expressed with the following general formulas (10) is mentioned as unsaturation group content monomers other than an acrylic-acid-alkyl-ester monomer, it is not limited to these.



R⁵ shows the univalent organic group or hydrogen atom except an alkyl group among [type. R³ is synonymous with said R³.]

[0050] The univalent organic group except the alkyl group in a general formula (10) means the univalent organic group except the alkyl group defined in a general formula (9). The univalent basis etc. which contain the alkyl group, the glycidyl group, and polyalkylene glycol which have substituents (for example, a halogen atom, a hydroxyl group, an isocyanate group, a phenoxy group, a furfuryl group, a reactive silicon group, etc.) other than a hydrocarbon group as such a univalent organic group are mentioned. As a compound expressed with a general formula (10). (Meta) Acrylic acid; Hydroxyethyl, (Meta) Hydroxyalkyl, such as acrylate. (Meta) Acrylate; Isocyanateethyl. (Meta) Isocyanate alkyls, such as acrylate. (meta-) acrylate; -- phenoxy alkyl (meta-) acrylate [such as 2-phenoxyethyl (meta-) acrylate,] -- furfuryl (hydrogenation) groups, such as furfuryl (meta-) acrylate and tetrahydrofurfuryl (meta-) acrylate. Have. (Meta) Acrylate; gamma-. (Methacryloxypropyl) Trimethoxysilane etc. (meta-) acryloxyalkyl alkoxysilane; -- glycidyl (meta-) acrylate; -- the acrylic ester (meta-) of polyalkylene oxide monoacors, such as methoxy polyethylene-glycol (meta-) acrylate, etc. are mentioned.

[0051] (Meta) As an acrylic-acid-alkyl-ester monomer and an unsaturation group content monomer which can be used together, a compound which was illustrated below besides what is expressed with the above-mentioned general formula (10) can be used. Namely, N-substitution or N,N-substitution (meta) acrylamide, such as N,N-dimethylacrylamide; Vinyl glycidyl ether, Unsaturated glycidyl ether, such as allyl glycidyl ether and methallyl glycidyl ether; Crotonic acid glycidyl, Monoalkyl monoglycidyl ester or diglycidyl ester of glycidyl ester; unsaturated dicarboxylic acid glycidyl; Styrene, Styrene monocarboxylic acid, such as cinnamic acid glycidyl and vinylbenzoic acid glycidyl; Styrene, Styrene monomers, such as alpha-methylstyrene and chlorostyrene; Acrylonitrile, Cyano group content monomers, such as 2,4-dicyano butene-1; Vinyl acetate, Vinyl ester system monomers, such as vinyl propionate; diene system monomer; olefin; halogenation olefin; unsaturated ester; vinyl ether, such as butadiene, isoprene, and chloroprene, etc. can be used.

[0052] The manufacturing method in particular of the polymer (B) in this invention is not restricted. (Meta) It can polymerize by a radical polymerization, anionic polymerization, cationic polymerization,

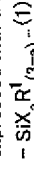
etc., using the above-mentioned unsaturation group content monomer which uses an acrylic-acid-alkyl-ester monomer as an essential ingredient. In this invention, as for a polymer (B), polymerizing a radical polymerization may be preferred, and the gestalt may be any of solution polymerization, an emulsion polymerization, suspension polymerization, and bulk polymerization.

[0053] When carrying out a radical polymerization, a radical polymerization initiator is usually added as a radical source of release to the above-mentioned unsaturation group content monomer. As a radical polymerization initiator which can be used in this invention, the polymerization initiator and a metal compound catalyst of a peroxide system, azo, or a redox system are mentioned. As a radical polymerization initiator, 2,2'-azobisisobutyronitrile, 2,2'-azobis 2-methylbutyronitrile, 2,2'-azobis (2,4-dimethylvaleronitrile), benzoyl peroxide, t-butyl peroxide, acetyl peroxide, diisopropyl peroxi dicarbonate, etc. can be illustrated. When activated with radiation or heat, a radical polymerization initiator is not necessarily required. It is preferred to perform the above-mentioned reaction at 20-200 °C (preferably 50-150 °C) for several hours - tens hours.

[0054] When compounding a polymer (B) by a radical polymerization in this invention, it is the purposes, such as molecular weight control, and a chain transfer agent may be added. As a chain transfer agent, alkyl mercaptan, such as n-dodecyl mercaptan, t-dodecyl mercaptan, and n-butyl mercaptan, an alpha-methylstyrene dimer, etc. can be used.

[0055] A polymer (B) may polymerize under the nonexistence of the hardenability constituent ingredient of this inventions other than a polymer (B), or may polymerize under existence. When polymerizing under existence of hardenability constituent ingredients other than a polymer (B), polymerizing under existence of an oxyalkylene polymer (A) is preferred. By polymerizing a polymer (B) under existence of an oxyalkylene polymer (A), mixed time and effort can be saved and the dispersibility of the polymer (B) in an oxyalkylene polymer (A) can also be raised. It is also considered that a part of unsaturation group content monomer for polymers (B) carries out graft polymerization in the middle of a polymerization at an oxyalkylene polymer (A), in such a case, a graft polymerization thing functions as a compatibilizer and the dispersibility of a polymer (B) improves more.

[0056] In this invention, it is preferred that a polymer (B) is a polymer including the acrylic-acid-alkyl-ester (meta) monomeric unit mentioned above, and it is a polymer which has a reactive silicon group expressed with a following general formula (1).



R¹, X, and a are synonymous with said R¹, X, and a among [type.]

[0057] When a polymer (B) has a reactive silicon group expressed with the above-mentioned general formula (1), in particular the number and the existence part of a reactive silicon group in the molecule of a polymer (B) are not restricted. The number of a reactive silicon group is just one or more, and the end or side chain of a polymer (B) molecule may be sufficient as an existence part, or they may be both an end and a side chain.

[0058] As a method of introducing the reactive silicon group expressed with the above-mentioned general formula (1), following (i) - the method of (iv) are mentioned to a polymer (B). The method of the following (i) - (iv) may be combined and may be performed.

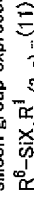
(i) How to use together the unsaturation group content monomer which has a reactive silicon group expressed with a general formula (1) in polymerizing an unsaturation group content monomer.

(ii) How to use the chain transfer agent which has a reactive silicon group expressed with a general formula (1) in polymerizing an unsaturation group content monomer.

(iii) How to use the initiator which has a reactive silicon group expressed with a general formula (1) in polymerizing an unsaturation group content monomer.

(iv) A method to which the compound which has a reactive silicon group which in polymerizing an unsaturation group content monomer uses together the unsaturation group content monomer which has a specific functional group, and is expressed with the specific functional group concerned, a reactant basis, and a general formula (1) is made to react.

[0059] The compound which is used in the method of the above-mentioned (i) and which is expressed with a following general formula (11) as an unsaturation group content monomer which has a reactive silicon group expressed with a general formula (1) is preferred.



R⁶ shows among [type the univalent organic group which has an unsaturation group. R¹, X, and a are

synonymous with said R^1 , X, and a.]

[0060]As a compound expressed with the above-mentioned general formula (11),

Vinylmethyldiethoxysilane, vinylmethyldiethoxysilane, vinyl methyl di chlorosilane,

Vinyltriethoxysilane, vinyltriethoxysilane, vinyl trichlorosilane, Vinylsilane, such as tris (2-

methoxyethoxy) vinylsilane; 3-acryloyloxypropylmethyldimethoxysilane, 3-methacryloyl oxypropyl

methyl dimethoxysilane, 3-acryloyloxypropyl trimethoxysilane, (meth)acryloyloxy silanes, such as 3-

acryloyloxypropyl triethoxysilane, 3-methacryloyl oxypropyl trimethoxysilane, and 3-methacryloyl

oxypropyl triethoxysilane, etc. can be mentioned. Especially in the above-mentioned compound, 3-

acryloyloxypropyl trimethoxysilane and 3-methacryloyl oxypropyl trimethoxysilane are preferred. the

above-mentioned compound comes out and requires using combining one sort or two sorts or more.

[0061]As for the unsaturation group content monomer which has a reactive silicon group expressed

with the above-mentioned general formula (1), it is preferred to consider it as 0.01 - 20 mass part

among the total monomer 100 mass part used for composition of a polymer (B).

[0062]As a chain transfer agent which has a reactive silicon group expressed with the above-

mentioned general formula (1) used in the method of the above-mentioned (ii), For example, gamma-

mercaptopropyltrimethoxysilane, gamma-mercaptopropylmethyl dimethoxysilane, gamma-

mercaptopropyl triethoxysilane, gamma-mercaptopropylmethyl diethoxysilane, The mercaptan

compound which has hydrolytic silyl groups, such as gamma-mercaptopropyltriethoxysilane, and

propenyloxy silane, $(CH_3O)_3Si-(CH_2)_3-Si(OCH_3)_3$ and

$(CH_3O)_3Si-(CH_2)_3-Si(OCH_3)_3$ are mentioned.

[0063]In [can use as an initiator the azo compound which has a reactive silicon group expressed with

the above-mentioned general formula (1) in the method of being the above-mentioned (iii), for

example, and] the method of the above-mentioned (iv), For example, the compound expressed with

the polymer (B) which has an isocyanate group, and the above-mentioned general formula (5) can be

made to react.

[0064]Although the molecular weight in particular of the polymer (B) explained above is not

restricted, it is preferred as Mn that it is 500-100000, and it is more preferred that it is 2000-13000.

When Mn of a polymer (B) exceeds 100000, workability tends to worsen, and when Mn is less than

500, it is in the tendency which becomes insufficient [weatherability].

[0065]When a polymer (B) has a reactive silicon group expressed with a general formula (1), since

combination arises between the reactive silicon groups in a polyoxalkylene polymer (A) at the time

of hardening, it becomes possible to raise intensity, weatherability, etc. of a hardenability constituent

after hardening. Since a polymer (B) with a reactive silicon group can be obtained to a molecular

terminal by the method of being (ii) using the chain transfer agent which has a reactive silicon group,

and the method of (iii) using the initiator which has a reactive silicon group, It becomes possible to

raise especially the extension characteristic of the hardenability constituent after hardening.

[0066]Next, the organic resin minute hollow body (C) in the hardenability constituent of this invention

is explained. As for the organic resin minute hollow body (C) in this invention, the mean particle

diameter which the husks wall comprised with organic resin says a spherical hollow body of 1 mm or

less. As for the mean particle diameter of an organic resin minute hollow body (C), 1-500

micrometers is preferred, its 1-250 micrometers are more preferred, and its 5-100 micrometers are

still more preferred. Although low molecular weight compounds, foaming agents, etc., such as low

boiling point hydrocarbon, may exist in the inside of the husks wall of an organic resin minute hollow

body (C), an organic resin minute hollow body (C) may expand with heating etc. in this case and mean

particle diameter may increase, the above-mentioned mean particle diameter means the mean

particle diameter before expansion.

[0067]In this invention, an usable organic resin minute hollow body (a minute hollow body is hereafter

called "balloon.") can be divided roughly into a thermosetting resin balloon and a thermoplastics

balloon. As a thermosetting resin balloon, a phenol resin balloon, an epoxy resin balloon, A urea resin

balloon is mentioned and a polyvinylidene chloride system resin balloon, a polystyrene balloon, a

polymethacrylate balloon, a polyvinyl alcohol balloon, and a styrene acrylic resin balloon are

mentioned as a thermoplastics balloon.

[0068]In this invention, the balloon which covered the surface of the above-mentioned thermoplastics

balloon with thermosetting resin, and the thermoplastics balloon which constructed the bridge can

also be used. It is usable also in the balloon which coated the surface of the above-mentioned thermoplastics balloon with inorganic powder, such as calcium carbonate, talc, and titanium oxide.

[0069]As a phenol resin balloon, PHENOLIC MICROBALLOONS provided by UNION CARBIDE can be

used. for example. It is usable in ECCOSPHERES VF-O provided with ECCOSPHERES EP provided

by EMERSON& CUMING by EMERSON & CUMING as a urea resin balloon as an epoxy resin balloon.

[0070]As a polyvinylidene chloride system resin balloon, SARAN MICROSPHERES provided by DOW

CHEMICAL, Expancel provided from Japanese phyllite, and the Matsumoto microsphere provided by

Matsumoto Yushi-Seiyaku can be used. As a polystyrene balloon, it is usable in DYLITE

EXPANDABLE POLYSTYRENE provided by ARCO POLYMERS and EXPANDABLE POLYSTYRENE

BEADS provided by BASF A.G. As a constructed type styrene acrylic acid balloon of a bridge, SX863

(P) provided by Japan Synthetic Rubber Co., Ltd. can be used. As a balloon which coated the surface

of the thermoplastics balloon with inorganic powder, such as calcium carbonate, talc, and titanium

oxide, the Matsumoto microsphere MFL series provided by Matsumoto Yushi-Seiyaku can be used.

[0071]In this invention, it is preferred to use a polyvinylidene chloride system resin balloon as an

organic resin minute hollow body (C). The polyvinylidene chloride system resin balloon refers to the

balloon (called a saran balloon.) in which a husks wall consists of polyvinylidene chloride system resin,

and, as for polyvinylidene chloride system resin, refers to the homopolymerization thing of a

vinylidene chloride, the copolymer of a vinylidene chloride, or these mixtures here. As monomers

other than the vinylidene chloride which constitutes the copolymer of a vinylidene chloride,

VCM/PVC, acrylonitrile, the acrylic-acid-alkyl-ester monomer expressed with a general formula (9)

(meta), the compound expressed with a general formula (10), etc. can be used, for example.

[0072]The hardenability constituent of this invention is a thing containing the oxalkylene polymer (A)

and polymer (B) which were explained above, and an organic resin minute hollow body (C). Although

such composition ratios in particular are not restricted, in this invention, it is preferred that a polymer

(B) is 1 - 300 mass part to oxalkylene polymer (A) 100 mass part, it is more preferred that it is 1 -

100 mass part, and it is preferred that it is especially 1 - 50 mass part. As for an organic resin minute

hollow body (C), it is preferred that it is 0.01 - 20 mass part to a total of 100 mass parts of an

oxalkylene polymer (A) and a polymer (B), it is more preferred that it is 0.05 - 10 mass part, and it is

preferred that it is especially 0.1 - 5 mass part.

[0073]The hardenability constituent of this invention can be obtained by compounding a polymer (B)

by an above-mentioned method apart from this oxalkylene polymer (A), and mixing these and an

organic resin minute hollow body (C), for example, after compounding an oxalkylene polymer (A) by

an above-mentioned method. After compounding an oxalkylene polymer (A), it can obtain also by

compounding a polymer (B) under existence of this polymer, adding an organic resin minute hollow

body (C) to this, and mixing. In the case of the latter, a polymer (B) may be compounded under

existence of an oxalkylene polymer (A) and an organic resin minute hollow body (C). An organic

solvent can be used in the case of composition or mixing, and it is possible after composition or

mixing to remove this organic solvent as occasion demands.

[0074]The hardenability constituent of this invention may contain additive components other than an

oxalkylene polymer (A), a polymer (B), and an organic resin minute hollow body (C), such as a bulking

agent, a hardening accelerator, an adhesive grant agent, a dehydrator, a thixotropic grant agent, a

solvent, a plasticizer, and an antiaging agent. The method in particular of adjusting the hardenability

constituent containing such an additive component is not restricted, but should just add an additive

component in once or several steps at the suitable stage after manufacture in the middle of

manufacture of a hardenability constituent. Hereafter, these additive components are explained.

[0075]First, the bulking agent which can be used for the hardenability constituent of this invention is

explained. In this invention, a bulking agent can be added to a hardenability constituent. Precipitated

calcium carbonate with a mean particle diameter of 1-3 micrometers manufactured as a bulking agent

with heavy calcium carbonate with a mean particle diameter of 1-20 micrometers and a

sedimentation method. The ocolloid calcium carbonate which carried out the surface treatment of the

surface with fatty acid or a resin acid system organic matter, Calcium carbonate [such as minor

nature calcium carbonate, J. fumed silica; --- sedimentation nature silica; --- surface silicization

silica pulverized coal; --- silicic acid anhydride; --- hydrous-silicic-acids; --- carbon black; ---

magnesium carbonate; --- diatomite; --- calcination clay; --- clay; --- talc; --- titanium oxide; ---

bentonite; --- ferric oxide; --- zinc oxide; --- active white; --- resin beads and wood flour, pulp, a cotton

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chip, mica, and the blacking wash farina — it rubs and fibrous fillers, such as powder state bulking agent, glass fibers, such as farina, graphite, aluminum impalpable powder, and the Flint powder, a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber, are mentioned.

[0076] These bulking agents may be used independently and may use two or more sorts together. In these, it is preferred to use calcium carbonate and especially the thing for which heavy calcium carbonate and colloid calcium carbonate are used together is preferred. The weight saving of a hardenability constituent and its cobwebbing nature of a constituent can be improved and workability can be raised. Although a hollow body may be used independently, it may use combining the bulking agent of others, such as calcium carbonate. The amount of the bulking agent used in this invention has 1 — 1000 preferred mass part to a total of 100 mass parts of an oxyalkylene polymer (A) and a polymer (B), and its 50 — 250 mass part is more preferred.

[0077] Next, the hardening accelerator which can be used for the hardenability constituent of this invention is explained. The crosslinking reaction of the reactive silicon group contained in the oxyalkylene polymer (A) in this invention advances, even if the compound which promotes a reaction does not exist, but, when a reactive silicon group is alkoxy silyl groups, for example, in order to make practically sufficient cure rate reveal, it is preferred to use a hardening accelerator.

[0078] As a hardening accelerator, 2-ethylhexanoic acid tin, naphtheneic acid tin, Divalent tin compounds, such as stearic acid tin; Dibutyltin dilaurate, Organic tin carboxylate like dialkyl tin dicarboxylates, such as dibutyltin diacetate, dibutyltin mono- acetate, and dibutyltin malate, or dialkoxo tin mono- carboxylate, The Suzuki rate compounds, such as dialkyl tin bisacetate/acetate and a JIARUKIRUSUZU monoacetate/acetate monoalkoxide, Tetravalent tin compounds, such as a silane compound and a dialkyl tin dialkyl sulfide, are mentioned.

[0079] As a Suzuki rate compound, dibutyltin bisacetate/acetate, dibutyltin bis-ethylacetate/acetate, a dibutyltin monoacetate/acetate monoalkoxide, etc. are mentioned. The tin compound which carry out heating mixing, and dibutyltin oxide and phthalic ester, such as dioctyl phthalate and phthalic acid diisooxonyl ester, were made to react as a reactant of dialkyl tin oxide and an ester compound, and was made liquefied is mentioned. In this case, as an ester compound, aliphatic series other than phthalic ester, ester of aromatic carboxylic acid, tetraethyl silicate, its partial hydrolysis condensate, etc. can be used. The compound which reacted or mixed these tin compounds with low molecule alkoxy silane etc. can also be used preferably.

[0080] As a curing catalyst which can be used in addition to a tin compound, Divalent bismuth compounds, such as organic-carboxylic-acid bismuth salt; Phosphoric acid, p-toluenesulfonic acid, Acetic acid, etc., such as phthalic acid and phosphoric acid di-2-ethylhexyl; A butylamine, Hexylamine, octylamine, decyl amine, lauryl amine, Aliphatic series monoamines, such as N,N-dimethyl- octylamine, ethylenediamine, Hexamethylenediamine, diethylenetriamine, triethylenetetramine, Aliphatic polyamine compounds, such as tetraethylenepentamine, an aromatic amine compound, Amine compounds, such as aminosilane coupling agents, such as alkanolamine, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, and 3-aminopropyl trimethoxysilane, are mentioned. Since their hardening facilitatory effect will improve if a divalent tin compound and a divalent bismuth compound are used together with the 1st class amine compound using together is preferred. The above-mentioned hardening accelerator can also be used combining one sort or two sorts or more. As for the addition of the hardening accelerator in the case of using a hardening accelerator, it is preferred to consider it as 0.1 — 10 mass part to a total of 100 mass parts of an oxyalkylene polymer (A) and a polymer (B).

[0081] Next, the adhesive grant agent which can be used for the hardenability constituent of this invention is explained. In this invention, an adhesive grant agent may be added to a hardenability constituent in order to improve an adhesive property. As an adhesive grant agent, silane coupling agents, such as (meth)acryloxy group content Silang, amino group content Silang, sulfinyl group content Silang, epoxy group content Silang, and carboxyl group content Silang, are mentioned.

[0082] As (meth)acryloxy group content Silang, 3-methacryloyl oxypropyl trimethoxysilane, 3-acryloyloxypropyl trimethoxysilane, 3-methacryloyl oxypropyl methyl dimethoxysilane, etc. are mentioned. As amino group content Silang, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-aminopropyl methyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl

trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl triethoxysilane, 3-ureido propyl triethoxysilane, N-(N-vinylbenzyl 2-aminoethyl)-3-aminopropyl trimethoxysilane, 3-anilino propyltrimethoxysilane, etc. are mentioned.

[0083] As sulfinyl group content Silang, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyl triethoxysilane, 3-mercaptopropylmethyl dimethoxysilane, 3-mercaptopropylmethyl dimethoxysilane, 3-glycidyloxypropyl trimethoxysilane, 3-glycidyloxypropylmethyl dimethoxysilane, 3-glycidyloxypropyl triethoxysilane, etc. are mentioned. As carboxyl group content Silang, 2-carboxyethyl triethoxysilane, 2-carboxyethyl phenylbis(2-methoxyethoxy)Silang, N-(N-carboxymethyl 2-aminoethyl)-3-aminopropyl trimethoxysilane, etc. are mentioned.

[0084] The reactant produced by making two or more sorts of silane coupling agents react may be used. As an example of a reactant, the reactant of amino group content Silang and epoxy group content Silang, the reactant of amino group content Silang and (meth)acryloxy group content Silang, the reactant of epoxy group content Silang and sulfinyl group content Silang, the reactant of sulfinyl group content Silang, etc. are mentioned. These reactants can be easily obtained by mixing a silane coupling agent and agitating in a room temperature — 150 °C temperature requirement for 1 to 8 hours. The above-mentioned compound may be used alone and may use two or more kinds together. The amount of the silane coupling agent used has 0 — 10 preferred mass part to a total of 100 mass parts of an oxyalkylene polymer (A) and a polymer (B).

[0085] In this invention, an epoxy resin can also be added as an adhesive grant agent. As an epoxy resin which can be added to the hardenability constituent of this invention, A bisphenol A-diglycidyl ether type epoxy resin, a bisphenol F-diglycidyl ether type epoxy resin, Fire retardancy type epoxy resins, such as a tetrabromobisphenol A-glycidyl ether type epoxy resin, Novolak type epoxy resin, a hydrogenation bisphenol A type epoxy resin, The glycidyl ether type epoxy resin of bisphenol A / propylene oxide addition, 4-glycidyloxy benzoic acid diglycidyl, phthalic acid diglycidyl, Diglycidyl ester system epoxy resins, such as tetrahydrophthalic acid diglycidyl and hexahydrophthalic acid diglycidyl, m-aminophenol series epoxy resin, a diaminodiphenylmethane system epoxy resin, Urethane modified epoxy resin, various cycloaliphatic-epoxy-resin, N, and N-diglycidyl aniline, N,N-diglycidyl o-toluidine, triglycidyl isocyanurate, Epoxy resins, such as an epoxidation thing of unsaturation polymers, such as glycidyl ether of polyhydric alcohol, such as polyalkylene glycol diglycidyl ether and glycerin, a hydantoin type epoxy resin, and petroleum resin. The vinyl system polymer containing an epoxy group, etc. are mentioned. The amount of [in the case of adding an epoxy resin] has 0 — 100 preferred mass part to oxyalkylene polymer (A)/100 mass part.

[0086] When adding the above epoxy resins to the hardenability constituent of this invention, the hardening agent (or curing catalyst) of an epoxy resin can also be added further. As such a hardening agent, triethylenetetramine, tetraethylenepentamine, Diethylenetriamine, Diethylenetriamine, N-aminoethyl piperazine, m-xylylene diamine, m-phenylenediamine, diaminodiphenylmethane, diaminodiphenyl sulfone, Blocked amine; polyamide resin; imidazole compound; dicyandiamide; boron trifluoride complex compounds, such as amine, such as isophoronediamine and 2,4,6-tris(dimethyl aminomethyl) phenol, those salts, or a ketimine compound; Phthalic anhydride, A hexahydrophthalic anhydride, a tetrahydrophthalic anhydride, a dodecyl succinic acid anhydride, carboxylic anhydride [such as a pyromellitic anhydride,]; — phenoxo resin; — carboxylic acid; — alcoholic; — the oxyalkylene system polymer (end amination polyoxypropylene glycol.) which averages the basis which can react to an epoxy group and it has at least one piece in intramolecular End carboxylation polyoxypropylene glycol etc.; The polybutadiene, the hydrogenation polybutadiene, the acrylonitrile butadiene copolymer in which the end was embellished with a hydroxyl group, a carboxyl group, an amino group, etc., Liquefied end functional group content polymers, such as an acrylic polymer, a ketimine compound etc. are mentioned. The amount of [in the case of using an epoxy resin hardener] has 0.1 to 300 preferred mass part to epoxy resin 100 mass part.

[0087] Next, the dehydrator which can be used for the hardenability constituent of this invention is explained. In this invention, in order to improve the storage stability of a hardenability constituent, a little dehydrators are added in the range which has an adverse effect on neither hardenability nor pliability — things can be carried out. As such a dehydrator, ORUTOGI acid alkyl; althmethyl acetate, such as methyl orthoformate and ethyl orthoformate, Althmethyl acid alkyls, such as althmethyl acetate; hydrolytic organic silicon compound; hydrolytic organic titanium compounds, such as methyl

trimethoxysilane, vinyltrimethoxysilane, a tetramethoxy silane, and a tetraethoxysilane, etc. are mentioned. Especially, vinyltrimethoxysilane from a point of a price and an effect and especially a tetraethoxysilane are preferred. In the 1 liquid combination which adds a curing catalyst etc. to the hardenability constituent of this invention, and is filled up with and used for a moisture-proof container, such a dehydrator especially is effective. As for the amount of the dehydrator used in this invention, it is preferred to consider it as 0.1 - 30 mass part to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0088]Next, the thixotropy grant agent which can be used for the hardenability constituent of this invention is explained. In this invention, a thixotropy grant agent can be added to a hardenability constituent. The lapet nature of a hardenability constituent is improved by addition of a thixotropy grant agent. As a thixotropy grant agent, hydrogenation castor oil, fatty acid amide, calcium stearate, zinc stearate, impalpable powder silica, organic acid processing calcium carbonate, etc. are mentioned. As for a thixotropy grant agent, it is preferred to carry out 0.5-10 mass-part addition to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0089]Next, the solvent which can be used for the hardenability constituent of this invention is explained. In this invention, a solvent can also be added to a hardenability constituent for the purpose of adjustment of viscosity, and the improvement in preservation stability of a constituent. As this solvent, aliphatic hydrocarbon, aromatic hydrocarbon, halogenated hydrocarbon, alcohol, ketone, ester, and ether are mentioned. By adding alcohol, the preservation stability of the hardenability constituent of this invention improves. Therefore, it is preferred to add alcohol, when carrying out the mothball of the hardenability constituent. As such alcohol, alkyl alcohol of the carbon numbers 1-10 of methanol, ethanol, isopropyl alcohol, isopentyl alcohol, hexyl alcohol, etc. is mentioned. As for a solvent, it is preferred to carry out 0.1-50 mass-part addition to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0090]Next, the plasticizer which can be used for the hardenability constituent of this invention is explained. In this invention, a plasticizer can also be added to a hardenability constituent. As a plasticizer, di-(2-ethylhexyl)phthalate, dibutyl phthalate, Phthalic ester, such as phthalic acid benzyl butyl ester and phthalic acid disononyl ester, Diocetyl adipate, Alcohol ester, such as aliphatic-carboxylic-acid ester, pentaerythritol ester, such as a succinic acid screw (2-methylnonyl), dibutyl sebacate, and butyl oleate; Triocetyl phosphate, Phosphoric ester, such as tricresyl phosphate; Epoxidized soybean oil, 4,5-epoxy cyclohexane-1,2-dicarboxylic acid-di-2-ethylhexyl, epoxy plasticizer [such as epoxy stearic acid benzyl], - chlorinated paraffin; - the hydroxyl group of polyether; polyoxypropylene glycols, such as polyester plasticizer; polyoxyalkylene polyols, such as polyester in which dibasic acid and dihydric alcohol are made to come to react. A polyether derivative which was closed by alkyl ether, Poly alpha-methylstyrene, Oligomer of polystyrene, such as polystyrene; oligomer, such as polybutadiene, Butadiene Acrylonitrile, polychloroprene, polyisoprene, polybutene, hydrogenation polybutene, and epoxidation polybutadiene, is mentioned.

[0091]Comparatively low-molecular plasticizers, such as the above-mentioned phthalic ester, have a large plasticizing effect. In the hardened material of the hardenability constituent which uses these low-molecular plasticizers while most generally being used from hypoviscosity-ization of a constituent having an effect. Since the translatability to the surface of a plasticizer is high, when using it as adhesives, an adhesive fall may pose a problem, and contamination of the hardened material surface or the adherend of the hardened material circumference may be produced, or it may have an adverse effect also on the weatherability of the hardened material itself. Therefore, when using such a low-molecular plasticizer, it is preferred to adjust content suitably in consideration of compatibility with a hardenability constituent, etc.

[0092]In this invention, it is preferred that Mn uses what is called 1000 or more polymeric plasticizers among the plasticizers illustrated above. In this case, a polymeric plasticizer and a low-molecular plasticizer may be used together, using only a polymeric plasticizer. By using a polymeric plasticizer, effects, such as reduction of the stain resistance of the surface of a hardened material or circumference stain resistance, drying improvement in the paint on a hardened material, and reduction of the stain resistance on the surface of a paint, are acquired, and it contributes also to improvement in weatherability. Epoxy plasticizers, such as 4,5-epoxy cyclohexane-1,2-dicarboxylic acid-di-2-ethylhexyl. When it is used combining divalent tin carboxylate and the 1st class amine especially as a hardening accelerator, after fixing by a compression state under a fixed condition, it is

effective in a hardened material with a returning large rate (compression recovery rate) when immobilization is canceled being obtained. The above-mentioned plasticizer may be used independently or may use two or more sorts together. The amount of the plasticizer used in this invention has 1 - 100 preferred mass part to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0093]Next, the antiaging agent which can be used for the hardenability constituent of this invention is explained. In this invention, an antiaging agent can be added to a hardenability constituent. As an antiaging agent, an antioxidant, an ultraviolet ray absorbent, light stabilizer, etc. are mentioned, and it is usable in the compound of a hindered amine system, a benzotriazole system, a benzophenone series, a benzoate system, a cyanoacrylate system, an acrylate system, a hindered phenol system, the Lynn system, and sulfur systems. It is preferred to use it especially or more [of light stabilizer, an antioxidant, and the ultraviolet ray absorbents] combining two. With such directions for use, antiaging effects can be raised as a whole taking advantage of each feature. Especially the thing for which two or more sorts chosen from the hindered amine light stabiliser of the 3rd class and the 2nd class, a benzotriazole system ultraviolet ray absorbent, a hindered phenol system, and a phosphite system antioxidant are specifically combined is effective. As for the amount of an antioxidant, an ultraviolet ray absorbent, and the light stabilizer used, it is preferred respectively that it is 0.1 - 10 mass part to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B), respectively. In less than 0.1 mass parts, when antiaging effects are not fully revealed and exceed ten mass parts, it is economically disadvantageous.

[0094]Next, additive components other than the above which can be used for the hardenability constituent of this invention are explained. In this invention, it is possible to add an air-oxidation hardenability compound and a photoresist compound to a hardenability constituent. Adhesion of weatherability and dust is improved by adding these compounds. As for these compounds, using together, although it may use independently is more preferred. In adding an air-oxidation hardenability compound, the amount used to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B) 0.1 - 50 mass part. As for the amount used, when adding a photoresist compound, it is preferred to consider it as 0.1 - 50 mass part to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0095]The alkyl resin produced by denaturalizing drying oil, such as tung oil and linseed oil, and drying oil as an air-oxidation hardenability compound. The acrylic polymer, silicone resin, polybutadiene which denaturalized with drying oil. The denaturation thing of diene system polymers, such as a polymer of diene of the carbon numbers 5-8 and a copolymer, and also these polymers, or a copolymer, a curing-in-air (malein-ized denaturation, boiled oil denaturation, etc.) polyester compound, etc. are mentioned.

[0096]Polyfunctional (meta) acrylate is mentioned as a photoresist compound, and as polyfunctional (meta) acrylate. Tetraethylene glycol diacrylate, pentaerythritol - doria - the acrylic ester (meta-) of polyhydric alcohol, such as KURETO and trimethylolpropane triacrylate, can be illustrated. This photoresist compound is a monomer and a polymer (B) including an acrylic-acid-alkyl-ester (meta) monomeric unit is distinguished.

[0097]In this invention, the compound which generates a trimethyl silanol by hydrolysis in a hardenability constituent can also be added as a modulus regulator. By adding such a compound, the modulus of the hardened material at the time of making a divalent tin compound and the 1st class amine compound into a hardening accelerator especially is reduced, and stickiness of the surface is also reduced. As a compound which generates a trimethyl silanol, trimethylsilyl ether, such as fatty alcohol and phenol, etc. can be used and there is an effect which hardens late, so that the acidity of alcohol is strong. By changing the kind of alcohol arbitrarily, adjustment of hardenability is also possible and the trimethylsilyl ether of alcohol of the plurality for the purpose can also be used simultaneously. Hexamethyldisilazane etc. can be used. The amount of [in the case used of using the compound which generates a trimethyl silanol] has 0.1 - 10 preferred mass part to a total of 100 mass parts of an oxalkylene polymer (A) and a polymer (B).

[0098]Organic colors, such as inorganic pigment; copper phthalocyanine blue, such as iron oxide, chrome oxide, and titanium oxide, and Phthalocyanine Green, can be added to a hardenability constituent besides the above-mentioned compound. Although a hardenability constituent is colored by adding paints, the effect of improvement in weatherability is also expectable besides it.

[0099] Surface appearance like a granite or granite can also be given by adding the microbody of the color of the constituent, and a different color to a hardenability constituent in order to give the design nature as sealant especially. It is also possible to add fire retardant, an antifungal agent, the flattening currently used for the paint use, etc.

[0100] As explained above, the hardenability constituent of this invention is characterized by including the oxyalkylene polymer (A) which has a reactive silicon group, a polymer (B) including an acrylic-acid-alkyl-ester (meta) monomeric unit, and an organic resin minute hollow body (C) as an essential ingredient.

[0101] Since the minute hollow body has very small specific gravity, it is assumed that the weight saving of a constituent becomes possible by making this contain, but in combination with the hardenability constituent which makes basic composition an oxyalkylene polymer and a polymer including an acrylic-acid-alkyl-ester (meta) monomeric unit, especially when an organic resin minute hollow body is used as a minute hollow body, it becomes possible to raise the degree of a weight saving. Namely, when the minute hollow body (for example, glass balloons indicated by the example of JP 5-86325A) which does not comprise organic resin is used as a minute hollow body, even if it makes content increase, when the minute hollow body which consists of organic resin is used to the grade of a weight saving becoming insufficient, the grade of a weight saving becomes high also with a comparatively small addition. Although the reason which this phenomenon produces is not necessarily clear, it is possible that the brittleness of a husks wall is high and destruction of a husks wall produces the minute hollow body which does not comprise organic resin in the middle of kneading, and it is assumed that this becomes insufficient [a weight saving].

[0102] The organic resin minute hollow body in the hardenability constituent of this invention not only enables improvement in a weight saving as mentioned above, but also enables the cobwebbing prevention and slump reduction in which achievement is difficult when minute hollow bodies, such as glass balloons, are used. Although the reason which this phenomenon produces is not necessarily clear, either, an organic resin minute hollow body, compared with minute hollow bodies, such as glass balloons, to a polymer including an oxyalkylene polymer and/or (meta) an acrylic-acid-alkyl-ester monomeric unit, compatibility is high and having done the strong interaction more is assumed.

[0103] Therefore, the hardenability constituent of this invention is suitably applicable as sealant, a water blocking material, adhesives, a coating agent, etc., and even if it is a use which is exposed outdoors to a rainstorm, sunlight, etc. for a long period of time, it can be used satisfactorily. Since the degree of a weight saving is high, while being able to attain the weight saving of the subject which applied the hardenability constituent of this invention, it contributes also to a cost cut.

[0104] When using for the above uses, the hardenability constituent of this invention can be made 1 liquid combination or 2 liquid combination. 1 liquid combination is the one-ingredient type which contains a hardened type oxyalkylene polymer and a hardening accelerator during the same combination, and is combination of the moisture curing type which is kept where hygroscopic surface moisture is intercepted, reacts to the moisture in the air at the time of use, and is hardened from the surface. On the other hand, 2 liquid combination is the two-ingredient type of the base resin which uses a hardened type oxyalkylene polymer as the main ingredients, and the hardening agent which uses a hardening accelerator as the main ingredients, and is combination of the reacting cure type reacted and hardened by kneading these at the time of use.

[0105]

[Example] Although explained still in detail about the suitable example of this invention hereafter, this invention is not limited to these examples. In the following examples of manufacture, examples, and comparative examples, a part means a mass part. Mn and Mw/Mn are calculated by GPC as above-mentioned.

[0106] (Example 1-1 of manufacture) Use propylene glycol as an initiator and Under existence of a zinchexaacyano cobaltate glyme complex compound catalyst, in the hydroxyl value conversion molecular weight produced by making propylene oxide react, Mw/Mn by 17000 to polyoxypropylene diol of 1.3. The methanol solution of sodium methoxide was added, scale loss pressing-down methanol was distilled off, and the terminal hydroxyl groups of polyoxypropylene was changed into sodium alcoholate. Next, the allyl chloride was made to react, the unreacted allyl chloride was removed and refined, and the polyoxypropylene which has an allyl group at the end was obtained. To this reactant, methyl dimethoxysilane which is a hydrosilyl compound was made to react under existence of a

platinum catalyst, and the polyoxypropylene (henceforth "P1") which has a methyl dimethoxy silyl group at the end was obtained. Mn of P1 was 20000 and Mw/Mn was 1.35.

[0107] (Example 1-2 of manufacture), putting 40 g of xylene into a reactor with an agitator, and keeping at 110 °C. To this, 3.3 g of methyl methacrylate, 16.7 g of butyl acrylate, 11.0 g of methacrylic acid octadecyl, 1.6 g of gamma-methoxypropyl trimethoxysilane, it was dropped over 3 hours, agitating the solution which dissolved V-59 (Wako Pure Chem make, 2,2'-azobis (2-methylbutyronitrile)) 0.4g in the mixture of 6.8 g of styrene, and 0.64 g of gamma-mercapto propyltrimethoxysilane under a nitrogen atmosphere. After the xylene solution which dissolved 0.3g of end back further V-59 of dropping was dropped over 30 minutes, heating churning was carried out at the temperature for 3 hours. After adding 120 g to the xylene solution of the obtained copolymer and carrying out agitation mixing of P1 to it for 30 minutes, xylene was distilled off under 100 °C.

decompression and the polymer (henceforth "Pa") was obtained.

[0108] (Example 1) The hardenability constituent of Example 1 was produced by the raw material and presentation (mass ratio) which are shown in following Table 1, namely, — as opposed to Pa of 100 copies — as a bulking agent — fatty acid processing colloid calcium carbonate (Shiraiishi industrial company make.) 75 copies of formation CCR of white gloss, and heavy calcium carbonate (Shiraiishi calcium company make.) As 75 copies of HOWAITON SB, and a plasticizer, 40 copies of di-2-ethylhexyl phthalate, As a thixotropy grant agent, DISUPARON #6500 (made by Kusumoto industrial company) 3 copy, Added the tinuvin 327 (made in Tiba Specialty Chemicals) 1 copy as an ultraviolet ray absorber, the ADEKA stub LA62 (made by Asahi Denka Kogyo K.K.) 1 copy was added as light stabilizer, the IRUGA NOx 1010 (made in Tiba Specialty Chemicals) 1 copy was added as an antioxidant, and it mixed uniformly. After carrying out kneading mixing of this enough at a room temperature with a 3 more paint roll, As an organic resin minute hollow body, 0.6 copy of Expancel 551DE (made by a Japanese phyllite company), Added 1.5 copies of N-(2-aminoethyl)-3-aminopropyl trimethoxysilane as an adhesive grant agent, three copies of vinyltrimethoxysilane was added as a dehydrator, one copy of dibutyltin bisacetylacetonate was added as a curing catalyst, it kneaded enough, and the hardenability constituent was obtained. * and a number were given to what used the abbreviation etc. for the raw material of the hardenability constituent in Table 1, and the details were shown in Table 3.

[0109] (Comparative example 1) Replaced with 0.6 copy of organic resin minute hollow body, and five copies of glass balloons (Tokai industrial company make, cell star Z-36) were used, and also the hardenability constituent was produced like Example 1. The raw material and the presentation (mass ratio) were shown in Table 1.

(Comparative example 2) An organic resin minute hollow body was not used, and also the hardenability constituent was produced like Example 1. The raw material and the presentation (mass ratio) were shown in Table 1.

[0110]

[Table 1]

配合	割合	1	2
重合体	Pa	100	100
充填剤	白炭化CCR*	75	75
	ホワイトンSB*	75	75
可塑剤	DOP*	40	40
チキン性付与剤	チキソロン#9500*	3	3
紫外線吸収剤	チズン827*	1	1
光安定剤	アチカスタブLA62*	1	1
酸化防止剤	イルガノックス1010*	1	1
脱泡性付与剤	シラン化合物*	1.5	1.5
脱泡剤	VTMS*	3	3
硬化触媒	DBTDA* ¹⁰	1	1
有機樹脂微小中空体	エクスパンセル551DE ¹¹	0.6	—
ガラスバルーン	セルスター-Z36 ¹²	—	5

[0111] Applied the constituent of Example 1 and the comparative examples 1-2 on the aluminum plate of 1-mm thickness so that it might be set to 5 mm in thickness, and recuperated oneself for seven

days under 60% of humidity at 20 **, the 5-mm-thick hardened material was made to form on said aluminum plate, and this was made into the specimen. The exposure examination was done for this specimen with the Suga Test Instruments Co., Ltd. make sunshine super long life weather meter, and the surface state of the specimen of 1000 hours, 1500 hours, and 1800 hours after was observed. x to which, as for the standard of evaluation, neither O-milkiness nor a crack is accepted and to which a white bluish mark and a crack are accepted a little [**]; It was presupposed that the white bluish mark and crack which were carried out clearly are accepted.

[0112]Next, applied the constituent of Example 1 and the comparative examples 1-2 on the aluminum plate of 1-mm thickness so that it might be set to 0.2 mm in thickness, and recuperated oneself for seven days under 60% of humidity at 20 **, the 0.2-mm-thick hardened material was made to form on said aluminum plate, and this was made into the specimen. The exposure examination was done for this specimen with the Suga Test Instruments Co., Ltd. make sunshine super long life weather meter, and the surface state of the specimen of 300 hours, 600 hours, and 900 hours after was observed.

The standard of evaluation presupposed that it is the same as that of the above.

[0113]The spatula piece nature at the time of sounding the constituent of Example 1 and the comparative examples 1-2 with the state where it does not harden, by a spatula was observed, and workability was evaluated. The standard of evaluation was made into O:cobwebbing nothing and those with x:cobwebbing. Based on JIS A1439, the vertical mold specimen estimated the slump (mm) at 50 ** using the constituent of Example 1 in the state where it does not harden, and the comparative examples 1-2. The specific gravity of the constituent (after hardening) of Example 1 and the comparative examples 1-2 was measured based on the A method of JIS K7112.

[0114]The result of the above-mentioned examination is summarized in the following table 2, and is shown. When thickness was thick (thickness: 5 mm), also in any when thickness is thin (thickness: 0.2 mm), the constituent obtained by Example 1 and the comparative examples 1-2 showed good weatherability, so that clearly from the result shown in Table 2. However, as for the hardenability constituent of Example 1, a cobwebbing was not accepted to the cobwebbing having been seen by the evaluation test of workability as for the hardenability constituent of the comparative examples 1 and 2.

[0115]In the hardenability constituent of Example 1, a lappet was not observed to the lappet having produced the hardenability constituent of the comparative examples 1 and 2 in the slump test. In the hardenability constituent of Example 1, although the amount of the minute hollow body (organic resin minute hollow body) used was 0.6 copy to 100 copies of Pa, low specific gravity was shown no less than 14.8% rather than the specific gravity of the unaddded minute hollow body hardenability constituent (comparative example 2), but. In spite of having used five copies of glass balloons for the hardenability constituent of the comparative example 1 to 100 copies of Pa as a minute hollow body, the reduction rate of the specific gravity from an unaddded hollow body hardenability constituent (comparative example 2) was only 5.6%.

[0116]

[Table 2]

	実数例		比較例	
	1	1	2	2
試験の 耐熱性(5mm厚) 結果	1000時間	O	O	O
	1500時間	O	O	O
	1800時間	O	O	O
耐熱性(0.2mm厚)	300時間	O	O	O
	600時間	O	O	O
	900時間	O	O	O
施工性(へら切れ性)		O	X	X
スランプ(mm)		0	2	5
硬化物の比重		1.21	1.34	1.42

[0117]

[Table 3]

番号	化学種
*1	阻熱性透明硬化カルシウム (白工工業社製)
*2	重炭酸カルシウム (白石カルシウム社製)
*3	フタル酸ジ-2-エチルヘキシル
*4	阻熱アミド (神保化学社製)
*5	ベンゾトリアゾール系紫外線吸収剤 (和光化学工業社製)
*6	ヒンダードアミン系光安定剤 (旭電化工業社製)
*7	ヒンダードフェノール系酸化防止剤 (和光化学工業社製)
*8	N-(2-エチルヘキシル)-3-アミノプロピルトリメトキシシラン
*9	ビニルトリメトキシシラン
*10	ジブチルスズビスアセチルアセトナート
*11	光り硬化ビニルデセン系樹脂バルーン (日本タタケ社製、比重: 0.036)
*12	ガラスバルーン (東洋工業社製、比重: 0.21)

[0118]

[Effect of the Invention]As explained above, according to this invention, a cobwebbing does not occur at the time of use, but the slump at the time of un-hardening is small, the weatherability over the long period of time after hardening is also excellent, and it also enables the degree of a weight saving to provide a hardenability constituent high enough further.

[Translation done.]